

# COATINGS. ENAMELS

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## PARTICULARS OF STRUCTURE AND PHASE FORMATION IN ZIRCONIUM-CONTAINING FRITS AND GLAZES

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A comprehensive investigation is made of the particulars of structure and phase formation in zirconium-containing frits and semi-fritted glaze coatings obtained with such frits. It is found that the high physical-chemical and decorative-aesthetic characteristics, most importantly the durability of the coatings (3–4), are the result of directed phase formation, a rational combination of crystalline opacifying phases and their uniform distribution in the glassy matrix, and the formation of a uniform glass crystal structure.

**Key words:** opacifying phases, structure formation, zirconium-containing coating, directed phase formation, durability, decorative-aesthetic characteristics.

The main objective of the present work is to obtain zirconium-containing, durable, semi-fritted, mat coatings for floor tiles, which can be used in locations with intense pedestrian traffic and, correspondingly, function under conditions of high abrasive wear. In addition, we posed the problems of introducing a minimal amount of frit, obtaining which is a quite energy-intensive process because of the high temperature required to make the glass granulate (1500°C), and developing a ceramic tile that is a competitive with its foreign analogs.

Since the final product is a semi-fritted, white, opacified, glass crystal glaze with a mat finish, the frit, just like a constituent component of the initial material, must conform to certain requirements. Specifically, during firing the frit must crystallize with an opacifying phase being formed (in our case zirconium compounds) and its melting temperature must be low in order to promote the formation of a liquid phase that intensifies the formation of the semi-fritted glaze coating.

At the first stage the experimental investigations included a study of structure and phase formation processes accompanying the heating of the zirconium-containing frit as a component of the initial composition of the glaze mix and intensifier of glaze formation in obtaining coatings.

The investigations were tied to the technological process for manufacturing floor tiles, which is used at the “Keramin”

JSC where the firing is conducted according to a fast, one-stage regime with maximum temperature  $1160 \pm 5^\circ\text{C}$ . Since different data are presented in the literature (USSR Inventor's Certificate Nos. 1126553 and 916454; RF Inventor's Certificate No. 94038478) [1], the amount of frit in the initial composition was determined experimentally — its content ranges from 5 to 90%.<sup>2</sup>

The frits were synthesized in the system  $\text{Na}_2\text{O} - \text{K}_2\text{O} - \text{CaO} - \text{MgO} - \text{B}_2\text{O}_3 - \text{Al}_2\text{O}_3 - \text{SiO}_2 - \text{ZrO}_2$ . Quartz sand, kaolin, dolomite, chalk, calcium and sodium carbonates, boric acid, and Zircobit ( $\text{ZrSiO}_4$ ) were used as a basis for making the initial composition to obtain frit.

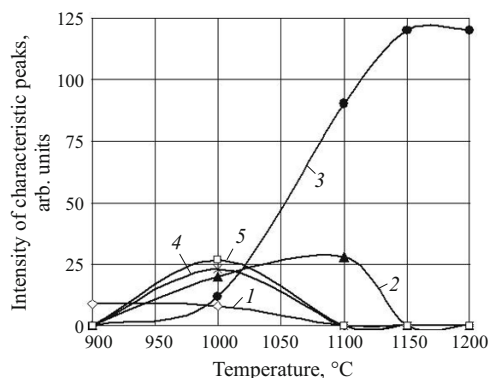
The frits were synthesized at  $1500 \pm 10^\circ\text{C}$  with 1-h soaking and poured into water to obtain a glass granulate and increase grindability. The frit designated as P was chosen on the basis of the technological characteristics, whiteness, and opacity for further investigation; the structure and phase formation of this frit was studied starting with its initial glassy state up to the completion of the crystallization processes.

The investigation included x-ray phase analysis with a Bruker (Germany) D 8 ADVANCE diffractometer. The recording was performed for angles  $2\theta$  ranging from 5 to  $80^\circ$  in  $0.1^\circ$  steps; the Joint Committee on Powder Diffraction Standards 2003 card file and Bruker's DIFFRAC PLUS software were used to identify the crystalline phases. A scanning electron microscope equipped with a microprobe analyzer

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<sup>2</sup> Here and below — content by weight.

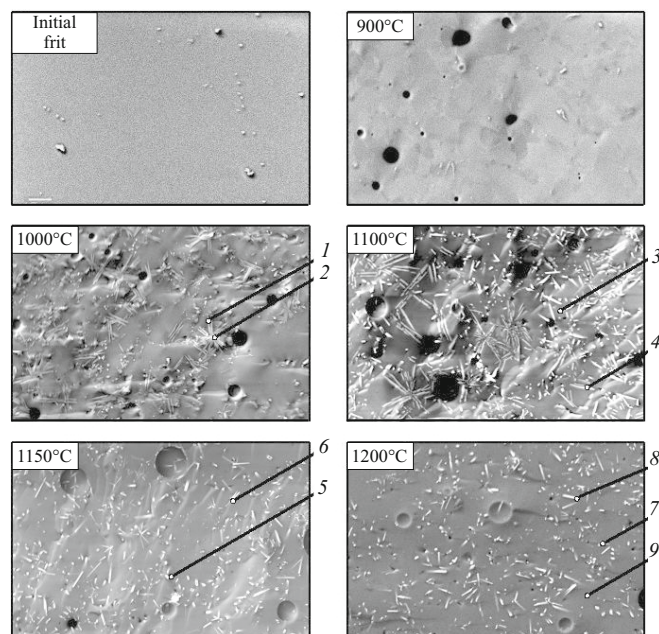


**Fig. 1.** Phase formation during heat-treatment of zirconium-containing frit P: 1) quartz; 2)  $\text{Ca}_2\text{ZrSi}_4\text{O}_{12}$ ; 3) zircon; 4) tetragonal  $\text{ZrO}_2$ ; 5) monoclinic  $\text{ZrO}_2$ .

(JEOL JSM 5610-LV, Japan) and  $\times 1000$  magnification was used to study the microstructure and chemical composition of the samples.

A visual assessment of the heat-treated samples of frit showed that the main structural – phase transformations occur in the temperature interval 1000 – 1200°C. For completeness, heat-treatment was performed in the temperature range 900 – 1200°C with a comparative study of the structure and phase of the composition of the initial glassy frit P.

The results of the study of the phase formation during heat-treatment of the zirconium-containing frit, which were obtained by analyzing the changes of the intensity of the main characteristic peaks of the phases formed, are displayed in Fig. 1. It was determined that the main opacifying phase ( $\text{ZrSiO}_4$ ) crystallizes via the formation of a series of intermediate compounds, specifically, tetragonal and monoclinic  $\text{ZrO}_2$ , as well as a solid solution of the type  $\text{Ca}_2\text{ZrSi}_4\text{O}_{12}$ , which diagnostics show in the temperature range 950 – 1150°C. The amount of  $\text{ZrSiO}_4$  increases actively at 1050°C and, correspondingly, the intensity of its characteristic peaks also increases. This process is accompanied by a simultaneous decrease of the intensity of the characteristic peaks due to intermediate phases right up to complete vanishing of the peaks, which is probably due to structural re-arrange-



**Fig. 2.** Electron micrographs of the cleavage surfaces of frit samples: 1 – 9) local sections of microprobe analysis.

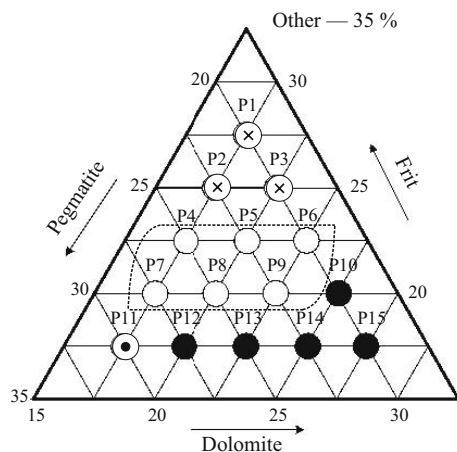
ments and interaction of the crystalline compounds, resulting in the formation of zircon.

The specification of the phase-formation and especially the structure-formation processes is supported by the electron-microscopic data obtained with local microprobe determination of the chemical composition of the glassy matrix phase and the crystalline phases which are the active opacifiers. In this connection, the structural rearrangements occurring in the glassy frit during heating are of great interest, since the zirconium-containing component ( $\text{ZrSiO}_4$ ) which is introduced dissolves during synthesis of the glass; this is supported by its virtually complete x-ray amorphousness.

Figure 2 shows the electron micrographs of the surface of the initial frit and the products of its heat-treatment; the points of local microprobe analysis of the chemical composition (Table 1) of the most characteristic regions consisting of

**TABLE 1.**

Oxide	Composition of the initial frit, %		Content of heat-treatment products in local sections, wt.%, at temperature, °C								
	computed	from surface	1000		1100		1150		1200		
			<i>1</i>	<i>2</i>	<i>3</i>	<i>4</i>	<i>5</i>	<i>6</i>	<i>7</i>	<i>8</i>	<i>9</i>
SiO <sub>2</sub>	66.23	64.78	64.24	64.55	66.99	52.68	52.24	48.65	55.13	48.88	68.50
MgO	2.39	2.91	1.54	0.94	3.32	1.57	2.07	1.67	1.60	0.89	2.49
CaO	10.53	10.33	9.75	10.97	9.87	6.14	6.20	4.86	7.87	6.27	11.38
K <sub>2</sub> O	2.48	1.64	2.09	1.46	1.70	1.09	1.03	0.94	1.30	0.87	2.18
Na <sub>2</sub> O	3.97	4.83	4.27	3.67	4.92	2.67	2.87	2.44	2.26	1.38	3.29
Al <sub>2</sub> O <sub>3</sub>	5.08	7.04	8.24	6.84	8.59	5.05	5.68	4.07	5.81	4.65	7.66
ZrO <sub>2</sub>	9.31	8.47	9.68	11.57	4.61	30.80	29.92	37.36	26.04	37.06	4.51



**Fig. 3.** Initial compositions of semi-fritted glazes and texture of the coatings obtained: ○) mat, silky, uniform spread; ●) mat, stony; ⊙) mat, silky, numerous fine pinholes; ⊗) mat, silky with low brightness.

the glassy phase, crystalline formations, centers of whisker growth, the whiskers themselves, and crystals of isometric form are also marked. The chemical composition of the initial frit, determined from the surface of the firing surface of the coating, correlates quite well with the computed composition as well as with the chemical composition of the glassy phase at the local points 3 and 9. The small deviations of the oxide content are due to partial pick-up of close-lying elements by the scanning electron beam.

The data in Table 1 agree with the results of phase-formation investigations (Fig. 1) and confirm the mechanism of the formation of the glass crystal structure of the frit during heating, including the formation of intermediate zirconium-containing crystalline phases (tetragonal and monoclinic  $\text{ZrO}_2$ ,  $\text{Ca}_2\text{ZrSi}_4\text{O}_{12}$ ).

Thus, in the temperature interval 1000–1100°C the chemical composition in local sections 1, 2, and 4 is represented by the compounds indicated and by a glassy phase whose composition corresponds to the section 4. The character of the structure, which is represented by zirconium crystals uniformly distributed over the surface (sections 5–8), changes substantially in the temperature interval 1100–1200°C because of intense formation of zirconium as a result of the interaction of the intermediate crystalline phases, re-

sidual quartz, and a liquid glassy phase. Diagnostics show no other crystalline phases right up to 1200°C. In this interval  $\text{ZrSiO}_4$  consists of morphologically arranged crystals, and as a result of the large difference between the refractive index of zircon ( $n = 2.2$ ) and that of the glassy component ( $n = 1.53$ ) the frit strongly scatters light, which gives maximum opacification. As follows from Fig. 1, in the temperature interval 1150–1200°C the frit consists of the two-phase system glass + zircon, so that the optimal temperature for heat-treatment of the frit was taken to be 1160°C.

The determination of the frit properties that are most important for glaze formation — the softening onset temperature, which is 650–660°C, and the CLTE —  $(61.5 - 61.8) \times 10^{-7} \text{ K}^{-1}$  (DIL 402 PC electronic dilatometer manufactured by Netzsch (German)) — showed that the synthesized frit could favorably affect the properties of the durable, mat, semi-fritted coating.

The experimental investigations performed at the second stage were directed toward direct synthesis of semi-fritted coatings, study of the phase and structural transformations in the process of their formation during firing, and determination of a complex of physical – chemical properties of coatings with serial experimental compositions. This made it possible to choose the optimal composition that satisfies the requirements for coatings to be used for decorating floor tiles.

The initial compositions containing dolomite, pegmatite, frit, and the remaining components (quartz sand, kaolin, alumina, Zircobit, zinc whites, wollastonite, refractory clay), whose total amount remained constant at 35%, are presented in Fig. 3. As one can see, coatings with a silky mat structure are formed in a limited range of the initial compositions.

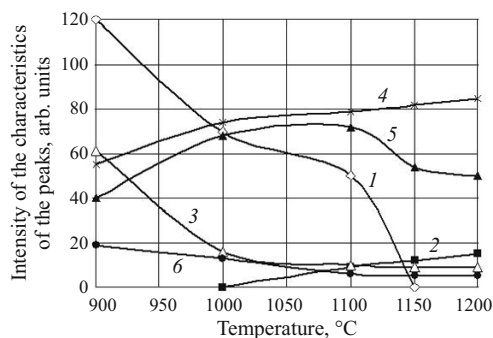
The most important properties of the coatings were determined in order to choose the optimal composition. The data in Table 2 show that the indicators of all coatings are close. This is probably because the phase formation occurring at the time the coatings are fired is identical because of the closeness of the oxide chemical composition, since the limits of the content of the main initial components in the glaze mix are relatively small (frit — 20.0–22.5%, pegmatite — 25.0–27.0%, dolomite — 17.5–22.5%).

The composition P4 is taken as optimal with respect to a complex of properties: highest microhardness (9100 MPa), Mohs hardness (9), and whiteness (92%). This coating has a mat silky texture and brightness 28%. The phase transformations occurring during the formation of the glaze in the temperature range 900–1200°C (Fig. 4) were studied for this coating, and conclusions about the particulars of their behavior on heating were drawn on the basis of a generalization of the data obtained for the frit P and initial composition P4.

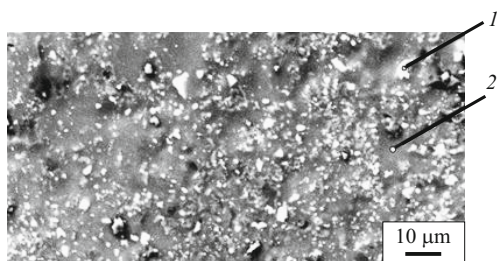
The phase formation process in a coating is different from that in frit. The following are observed at 900°C:  $\alpha$ - $\text{SiO}_2$  quartz, åkermanite  $\text{Ca}_2\text{Mg}(\text{Si}_2\text{O}_7)$ , zircon  $\text{ZrSiO}_4$ , corundum  $\alpha$ - $\text{Al}_2\text{O}_3$ , and diopside  $\text{CaMg}(\text{Si}_2\text{O}_6)$ .

**TABLE 2.**

Composition	Microhardness, MPa	Mohs hardness	CLTE, $10^{-7} \text{ K}^{-1}$	Whiteness, %	Brightness, %
P4	9100	9	63.2	92	28
P5	9050	9	63.2	91	32
P6	9060	8	63.6	90	37
P7	9060	9	63.9	90	30
P8	9080	9	62.4	90	34
P9	9090	8	62.6	90	34



**Fig. 4.** Phase formation during heat-treatment of the initial composition P4 in the process of obtaining a glaze coating: 1) quartz; 2) anortite; 3) åkermanite; 4) zircon; 5) diopside; 6) corundum.



**Fig. 5.** Electron micrograph of the cleavage surface of a P4 coating: 1, 2) local sections of microprobe analysis.

In the temperature interval 900 – 1000°C the intensities of the diffraction peaks of  $\alpha$ -quartz and åkermanite increase quite rapidly and the intensities of the zircon and diopside peaks increase smoothly. A similar process is also observed in the temperature interval 1000 – 1100°C, but in contrast to the preceding interval a new crystalline phase is observed to appear — monoclinic anortite  $\text{Al}_2\text{Ca}_{0.5}\text{Si}_3\text{O}_{11}$ , but apparently only a small amount. The largest changes of the phase composition occur in the temperature interval 1100 – 1150°C. There is virtually no quartz, the intensities of the diopside peaks decrease, and the intensities of the characteristic peaks due to zircon continue to increase. A further increase of the firing temperature of the composition increases to 1200°C does not contribute any great changes into the phase-formation process.

Therefore, the phase composition of the coating P4 at the optimal firing temperature  $1160 \pm 5^\circ\text{C}$  is represented by the main crystalline phases — zircon and diopside; the auxiliary phases are anortite, åkermanite, and corundum, which are present in small amounts. Unlike glaze, the phase composition of frit heat-treated according to a similar regime is represented solely by zircon (see Fig. 1) uniformly distributed in a glassy matrix (see Fig. 2).

During the coating formation process a rational combination of crystalline and cementing glassy phases is reached at  $1160 \pm 5^\circ\text{C}$ ; this gives a dense uniform structure for the durable, glass crystal, glaze and the required degree of opaci-

**TABLE 3.**

Oxide	Content, wt.%			
	crystal (section 1)	glass phase (section 2)	coating surface	computed composition
$\text{SiO}_2$	35.61	58.72	54.15	50.58
$\text{Al}_2\text{O}_3$	4.28	16.50	18.70	20.28
$\text{MgO}$	0.92	3.92	4.46	4.79
$\text{CaO}$	2.62	9.13	10.56	9.00
$\text{K}_2\text{O}$	0.81	3.41	2.58	2.62
$\text{ZnO}$	0.97	3.43	2.69	3.30
$\text{ZrO}_2$	54.05	3.26	5.31	5.78
$\text{B}_2\text{O}_3$		Not observed		1.89
$\text{Na}_2\text{O}$	0.74	1.64	1.53	1.76

fication. An electron micrograph of the cleavage surface of the P4 coating is displayed in Fig. 5; the points of local microprobe analysis of the chemical composition (Table 3) of the crystalline and glassy sections are indicated. It is clearly seen that the crystalline formations of the opacifying phases are uniformly distributed over the surface; this creates a high degree of opacification and a mat surface texture.

The data in Table 3 confirm the results of the study of the structural-phase transformations and show that a high degree of opacification of the coating P4 is attained as a result of the uniform distribution of zircon crystals in the glassy matrix and that the required properties obtain because the content of the crystalline and glassy phases, which form the crystalline structure of the glaze obtained, is optimal.

Floor tiles, which were engobed by pouring and then depositing a 0.3 mm thick layer of P4 coating, were used to perform tests under the conditions at “Keramin” JSC. After drying at  $100 \pm 10^\circ\text{C}$  to residual moisture content not exceeding 0.5% the tiles were subjected to fast high-temperature firing in an RKS-1650 gas-flame furnace in a conveyor production line at temperature  $1160 \pm 10^\circ\text{C}$  for  $43 \pm 1$  min.

The P4 coating obtained under real manufacturing conditions was characterized by a mat, silky, surface texture. The microhardness was 9100 MPa, the Mohs hardness was 7 – 8, the brightness and whiteness were 10 – 15 and 83 – 89%, respectively, and the CLTE was  $(67 - 72) \times 10^{-7} \text{ K}^{-1}$ . High bonding strength in the glaze-ceramic system was attained by matching the CLTE of the glaze coating to that of the ceramic base. The heat-resistance and chemical stability of the glaze coating also conform to standards. An advantage of the synthesized semi-fritted P4 coating is its high durability, ranked as 3 – 4, which makes it possible to recommend this coating for use in manufacturing.

## REFERENCES

1. G. V. Lusachuk, et al., *Glass Crystal Coatings on Ceramic* [in Russian], Kharkov (2008).